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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The mechanisms of oxide growth on InP, GaP, GaAs and InGaAs were investigated and their electrical properties measured. Islands were observed as the initial stage of anodization of InP and GaAs but the details of the growth on the two materials are different. The thermal oxides of InP and GaP also differ in composition and surface topography. InP forms bubbles and GaP has pits under the oxide. Traps at the deposited insulator/InP interface were also investigated. Originators.

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Growth Mechanisms and Properties of the Thermal

and Anodic Oxides of the III-V Compound Semiconductors

Final Report

By

C.W. Wilmsen

March 1985

U.S. ARMY RESEARCH OFFICE

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Colorado State University

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I. Statement Of The Research Problem

Discrete and integrated device structures on the III-V compounds require dielectric films for gate and field oxides, annealing caps and for passivation. Deposited insulators, such as SiO_2 and Al_2O_3, have an inherent mismatch with the substrate, can damage the surface during deposition and can dope the substrate during heat treatment. The grown oxides more naturally accommodate the surface defects and thus have a strong appeal.

This research program sought to determine many of the mechanisms involved in III-V growth, the changes which occur during heat treatment and to investigate the causes of electrical instabilities at the interface. Understanding these fundamentals has lead to better application of oxidation and how to control the interface. Four substrate materials were investigated; InP, GaAs, GaP and InGaAs with primary emphasis placed on InP.

Most of the experimental research utilized surface analysis techniques such as x-ray photoemission spectroscopy (XLS), ultraviolet photoemission spectroscopy (UPS) and secondary electron microscopy (SEM).

II. Summary Of The Most Important Results

The results given below are organized by process technique with substrate materials as sub-topics.

A. Thermal Oxidation

InP

The thermal oxides of InP were investigated to determine the chemical composition as a function of depth, the surface morphology, the crystalline structure and the direction of oxide growth. It was determined that the compositional profiles and surface topography changed dramatically above a growth temperature of $620^{\circ}C$ in 1 atm dry oxygen. Below this temperature the surface is relatively smooth and the interface has deposites of elemental phosphorous. The

oxide is composed of a mixture of In_2O_3 and $InPO_4$ with an increased $InPO_4$ with no detectable elemental phosphorus at the interface. This behavior was believed to occur by the softening of the oxide layer due to the rapid release of energy from the exthothermic oxidation. Any elemental phosphorus creates a pressure beneath the soft oxide. This causes bubbles to form. The diffusion rate of P in the soft oxide is much greater than before and thus the oxide film becomes predominately $InPO_4$.

The above data argues in favor of growth by the out diffusion of In and a slower out diffusion of P. O_2 is thought to diffuses only slowly. In order to test this hypothesis and to alter the growth kinetics, oxides were grown in high pressure atmospheres. Oxide films grown in a high pressure (500 atm) ambient were found to contain no elemental P but rather P_2O_5. This is evidence that the O_2 is driven into the film where it oxidizes the elemental P. The oxide film thus becomes layered. Oxidation in high pressure steam in H_3PO_4 yields different results indicating that the diffusing oxidant molecules changes the reaction kinetics. No difference was observed for growth at 1 atm in these ambients. Models for this oxide growth have not been worked out at present.

GaP

In principle the thermal oxidation of GaP should be very similar to that of InP. However, this was not found to be the case, e.g. the GaP oxide composition was found to be uniformally $GaPO_4$ for all growth temperatures and the growth rate in steam is 10 times that in dry O_2. In addition, no bubbles were observed on the GaP oxides but rather large pits framed under the oxides grown in dry O_2 but none for the steam grown.

A detailed study of the pits revealed a progression of shapes and sizes starting with small vertical wall pits aligned with the substrate crystalline planes. These change to rounded channels which winded around under the oxide (Figure 1).

InGaAs

The composition of these oxides follow from that previously observed on GaAs and InAs. The oxide bulk is a mixture of Ga_2O_3 and In_2O_3 with very little arsenic oxide. The As collects at the interface in elemental form. The growth rate fall midway between that of InAs and GaAs thus the out diffusion of In and Ga probably controls the growth.

B. Anodic Oxidation

GaAs

When GaAs is anodized at constant current it is convenient to record the cell voltage versus time. After an initial step in voltage there is a relatively flat portion of the curve which had been thought to be caused by island formation. We investigated this island formation by studying transmission electron micrographs of carbon replicas of the surface. These produced fine details of the islands and the nuclei as sown in Figure 2. The following observations were made.

- The nucleation process does not occur only in the initial stage but continued until the entire surface was covered with oxide.

- The islands grow to a thickness of ~200Å which occurs when the individual island area ~$0.1\mu^2$

- When the islands touched, they grew together and did not have a liquid like coalesence.

- The edges of the islands were very rough but clearly identifable.

The above data shows that continuous oxide layers less than 200Å thickness cannot be formed, at least by the standard process.

InP

The island growth of InP anodic oxides was found to be different from that of GaAs in that they had very smooth edges and tended to form in lines. All the islands were the same size and no small islands or nuclei were observed. This indicates that all the nuclei form at one time during an initial stage. While the

islands as InP appear to grow to approximately the same height as GaAs the islands were difficult to observe in the microscope since the edges were not abrupt.

The composition of the thicker InP anodic oxides were determined by x-ray photoelectron emission profiling to be a mixture of P_2O_5 and In_2O_3, which is different from the thermal oxides. The P_2O_5/In_2O_3 ratio could be varied in a controlled manner by adjusting the pH and the electrolyte composition. The composition ratio was correlated to electrical measures which strongly suggested the oxide was composed of small islands of one compound inbedded in a matrix of the other. since the In_2O_3 is a conductor and the P_2O_5 is an insulator, varying the ratio caused a very large change in the electrical resistance. For a small P_2O_5/In_2O_3 ratio, the current was carried by electron percolation through the maze of islands but for longer ratios the electrons must tunnel from island to island.

While the "as grown" anodic oxide can have a very high resistivity, $\sim10^{16}$ohm-cm, the P_2O_5 in the films readily absorb water which greatly reduces the resistivity. Annealing the as grown films partial converts the mixed oxide to $InPO_4$ but annealing at $650^{\circ}C$ cause the film to peal away from the substrate, rendering it useless as a protective coating.

Another type of anodization holds more promise. This technique forms a double layer anodic oxide film by anodizing a previously deposited aluminum film and the underlying InP substrate. While the same anodic process is followed the routine oxide has been found to be $InPO_4$ and not a mixture of P_2O_5 and In_2O_3. This oxide yields a high quality interface which may be suitable for device applications since it is stable in air and has a low interface state density. The resistivity of the double layer was found to be lower than the same single layers. This appears to be due, at least in part, to the migration of In through the outer layer of Al_2O_3.

C. Plasma Oxidation

InP

When SiO_2 is deposited on InP by the plasma enhanced CVD process, the excited O_2/N_2O may enhance the InP oxidation rate. Thus, this process could lead to a thicker interfacial oxide. This enhancement was charaterized by comparing the oxide thickness resulting from the exposure of plasma to that of a normal thermal oxide. For these tests a plasma enhanced CVD chamber was used but no SiH_4 was introduced into the chamber. Placing an InP wafer at the mouth of the plasma tube resulted in a rapid growth of oxide above $150^{\circ}C$ while placing the wafer well away from the plasma tube yielded little change from the normal thermal oxidation but increases rapidly above $350^{\circ}C$. There was, however, an initial fast rise in growth rate which saturated at $\sim 10\text{Å}$ thicker than without the plasma. The composition of the plasma enhanced films was very similar to that of the thermally grown oxide.

D. Interfacial Trapping

InP MOSFETs fabricated with a deposited gate dielectric have a drift in the drain current. The magnitude of the drift varies from very fast (seconds) to very slow (hours). It is thought that the drift is caused by traps in either the deposited dielectric or in the interfacial native oxide. We have investigated traps in both of these.

The XPS compositional profiles of thin native oxides on InP indicate that the inner most layer is primarily $InPO_4$ and the outer layer is a mixture of $InPO_4$ and In_2O_3. We have used surface analytical techniques to measure the band gap and electron affinity of $InPO_4$ and In_2O_3 in relation to the InP substrate. The band gap of $InPO_4$ was determined to be 4.5eV with the conduction band edge ~ 1.2eV above that of InP. The conduction band of In_2O_3 is only slightly above the conduction band of InP. Thus, the In_2O_3 can act as a trap for inversion layer electrons in InP. Using this as a model, calculations were made and compared to

published electrical data. A very close fit could be obtained by adjusting the oxide layer thickness. Electron loss spectra (ELS) from the native oxide indicated the presence of the In_2O_3 trap but no other intrinsic level. Thus, we concluded that there are no traps in the native oxide other than In_2O_3.

ELS and ultraviolet photoelectron spectroscopy (UPS) were used to identify traps in deposited SiO_2. Traps associated with Si-Si and Si-O bands were observed but these were too low in the band to yield the drain current drift. The study of impurity traps are presently being pursued.

III. List of Publications Resulting from this Contract

1. Initial States of anodic oxidation of GaAs, W. H. Makky, F. Cabrera, K. M. Geib and C. W. Wilmsen, J. Vac. Sci. Technol., 21, 417 (1982).

2. Island state of InP anodization, W. H. Makky and C. W. Wilmsen, J. Electrochem. Soc., 130, 659 (1983).

3. Oxidation of InP in a plasma-enhanced chemical vapor deposition reactor, J. F. Wager, W. H. Makky, C. W. Wilmsen and L. G. Meiners, Thin Solid Films, 95, 343 (1982).

4. High temperature annealing of InP anodic oxides, M. Fathipour, W. H. Makky, J. McLaren, K. M. Geib and C. W. Wilmsen, J. Vac. Sci. Technol., A1, 662 (1983).

5. Surface topography of oxides on InP thermally grown at high temperatures, J. J. McLaren, A. Nelson, K. M. Geib, R. Gann and C. W. Wilmsen, J. Vac. Sci. Technol., A1, 1486 (1983).

6. Estimation of the band gap of $InPO_4$, J. F. Wager, C. W. Wilmsen and L. L. Kazmerski, Applied Phys. Lett., 42, 589 (1983).

7. Composition and structure of thermal oxides of InP, A. Nelson, K. M. Geib and C. W. Wilmsen, J. Appl. Phys., 54, 4134 (1983).

8. New model for slow current drift in InP metal-insulator-semiconductor field effect transistors, S. M. Goodnick, T. Hwang and C. W. Wilmsen, Appl. Phys. Lett., 44, 453 (1984).

9. Thermal oxidation of GaP, Y. Kato, K. M. Geib, R. G. Gann, P. R. Brusenback and C. W. Wilmsen, J. Vac. Sci. Technol., A2, 588 (1984.

10. Influence of interfacial structures on the electronic properties of SiO_2/InP MISFET's, J. Vac. Sci. Technol., B2, 516 (1984).

11. High pressure thermal oxide/InP interface, C. W. Wilmsen, K. M. Geib, R. G. Gann, J. Costello, G. Hryckwan, R. J. Zeto, J. Vac. Sci. Technol., in press.

IV. Personnel Supported by the Project

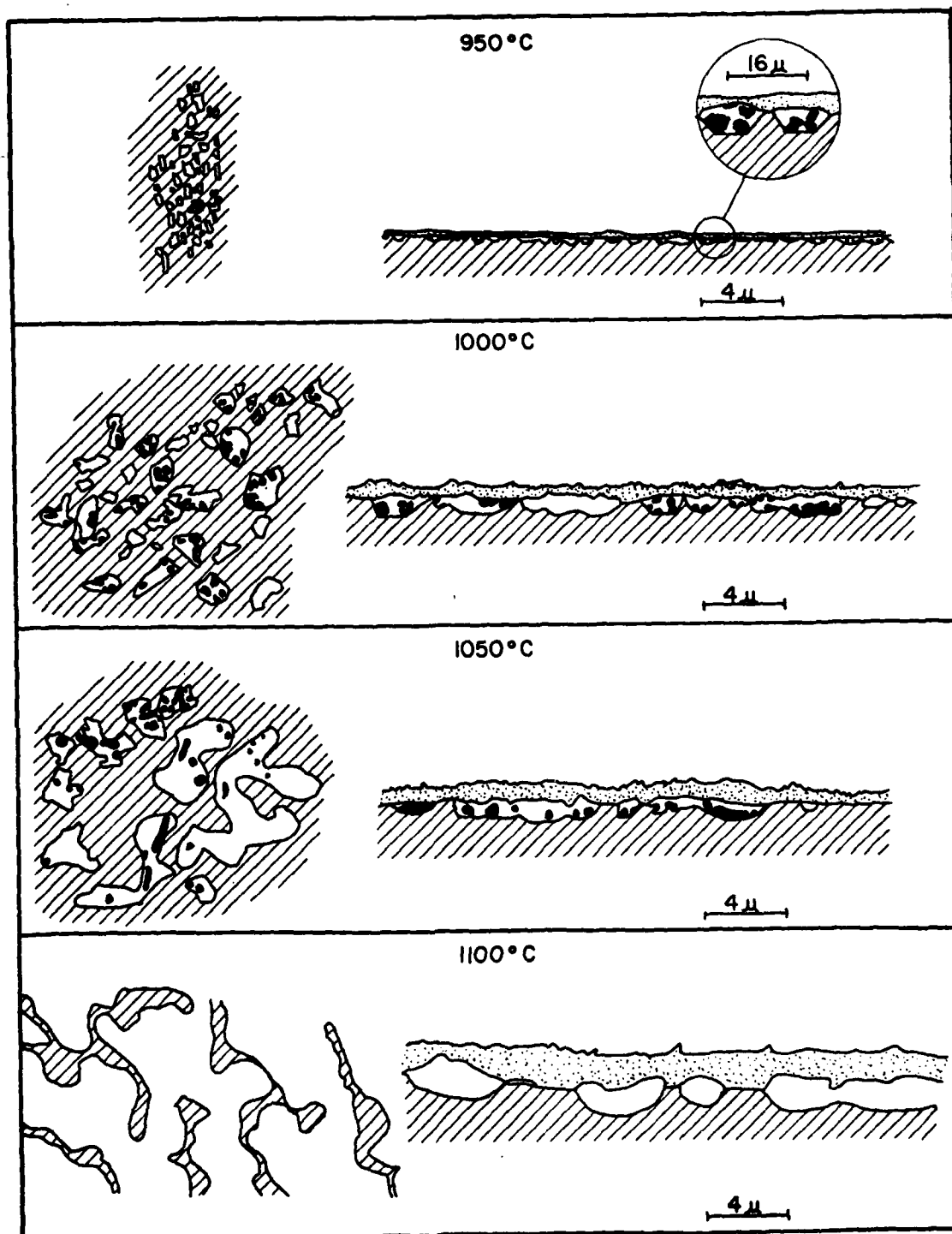|		
C. W. Wilmsen	–	Principal Investigator
K. M. Geib	–	Research Associate
S. M. Goodnick	–	Research Associate/Post Doc.
A. Nelson	–	Awarded MS degree
W. Makky	–	Awarded Ph.D. degree
K. Kato	–	Awarded MS degree
R. R. Chang	–	Awarded MS degree
Y. D. Lin	–	Awarded MS degree

Figure 1. Pits under the thermal oxide of GaP.

Figure 2.   Anodic oxide islands on GaAs grown in tartaric acid
              electrolyte, pH = 7 with strong light.
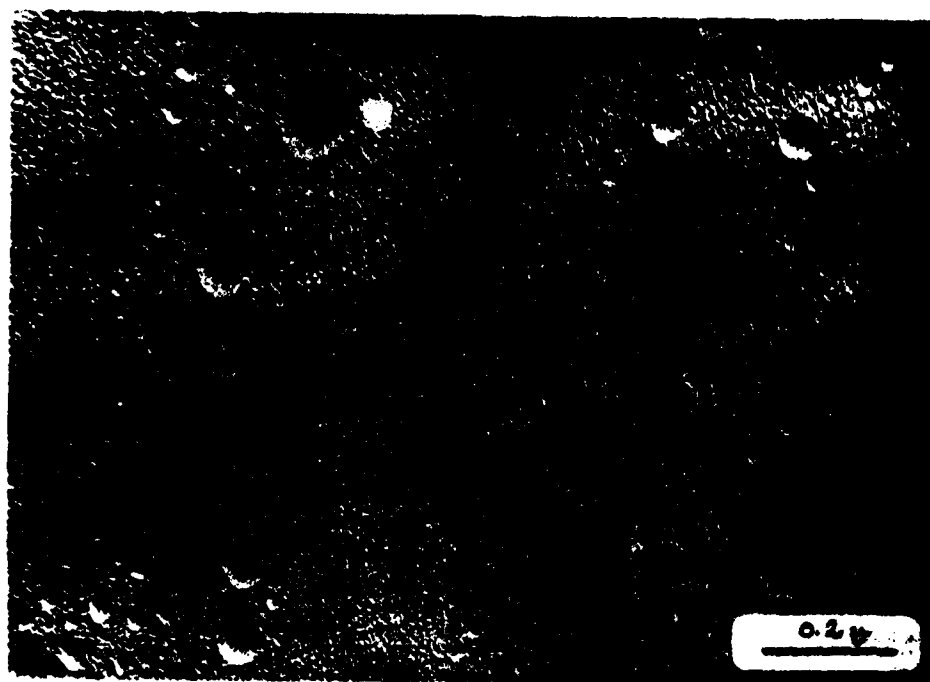

Figure 3.   Anodic oxide islands on InP formed by dipping the InP
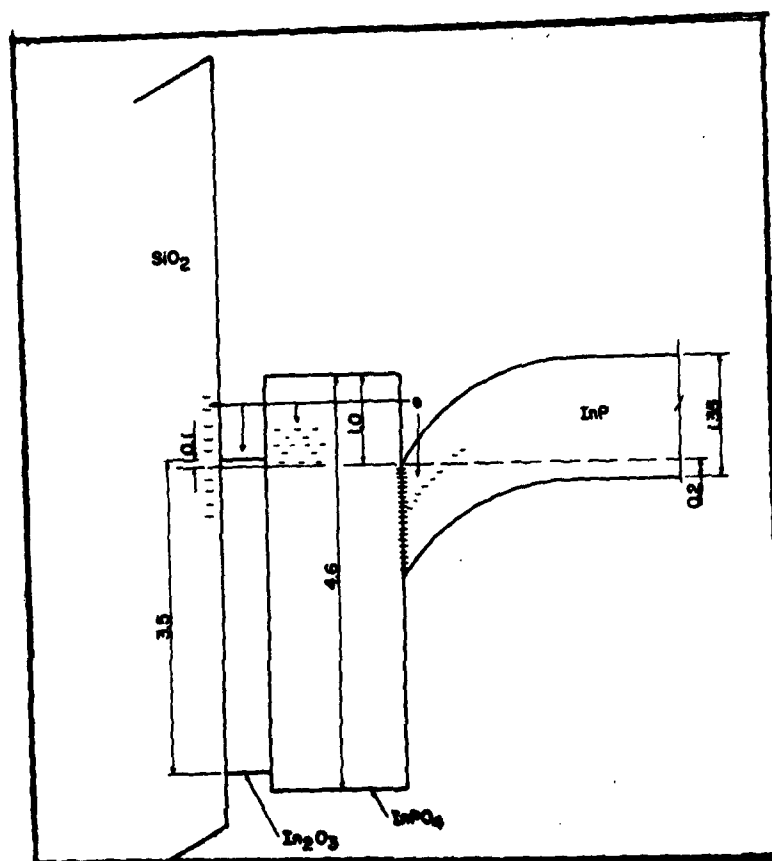   substrate in tartaric acid electrolyte, pH = 7.

Figure 4. An energy band diagram for the SiO_2/InP
system depicting possible trap sites in
the SiO_2, and In_2O_3 intermediate layer,
and in the bulk native oxide. The width
of the native oxide is exaggerated for
clarity.

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